

Polarization-based calculation of the dielectric tensor of polar crystals

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We present a novel method for the calculation of the static and electronic dielectric tensor of polar insulating crystals based on concepts from the modern theory of dielectric polarization. As an application, we present the first ab initio calculation of the dielectric constants in the wurtzite III-V nitrides AlN, GaN, and InN.

The modern quantum theory of polarization in dielectrics has been formulated only in recent years [1]. This development has opened a new era in the first principles theory of ferroelectricity and pyroelectricity [2]. The new theory has been used successfully to calculate, in a well defined and computationally efficient way, the macroscopic polarization changes induced by perturbations other than an electric field. Examples of such perturbations are e.g. lattice vibrations [2], ferroelectric distortions [2], and piezoelectric deformations [3,4], whereby the quantities being calculated are typically dynamical Born charges, spontaneous polarization, and piezoelectric constants.

So far, no direct attempt has been made towards the goal of determining the dielectric tensor (which of course quantifies the response to an external electric field) using polarization theory. In this Letter we present a novel method for calculating the static dielectric tensor of a crystal based on concepts from polarization theory; in particular, the method rests entirely on the evaluation of the dielectric polarization in zero field via the geometric quantum phase approach [1]. The method works in any polar material, i.e. any material having infrared-active zone-center modes. As an application, we provide the first (to our knowledge) determination of the dielectric constants ε_{\parallel} along the (0001) axis for the wurtzite III-V nitride compounds AlN, GaN, and InN.

The current method of choice for dielectric response calculations is Density Functional Perturbation Theory (DFPT) [5], a general and powerful approach to response properties. The method presented here, besides its different foundations, is less general but considerably simpler to implement than DFPT, and it may become a useful alternative.

The static dielectric tensor – The calculation of the dielectric tensor is highly non trivial, because it entails the determination of the electronic, as well as vibrational and elastic-piezoelectric, responses to an external electrostatic field. The elements of the dielectric tensor are

$$\varepsilon_{ij}^0 = \delta_{ij} + 4\pi \frac{dP_i}{dE_j}, \quad (1)$$

where \mathbf{E} is the screened macroscopic electrostatic field and \mathbf{P} the macroscopic polarization resulting from the response of the electronic and ionic degrees of freedom. In the Born-Oppenheimer approximation the macroscopic polarization \mathbf{P} in the presence of a generic strain or electrostatic perturbation can be conveniently expressed as $\mathbf{P} = \mathbf{P}^0 + \mathbf{P}^{\text{lat}} + \mathbf{P}^{\text{E}}$, the sum of the spontaneous polarization \mathbf{P}^0 of the equilibrium structure in zero field, the polarization \mathbf{P}^{lat} induced by lattice response, and the electronic screening polarization \mathbf{P}^{E} . In the linear regime and using Voigt notation, the two latter components can be expressed in terms of the lattice structure distortion and screened electric field as

$$P_i^{\text{lat}} = \sum_l e_{il}^{(0)} \epsilon_l + \frac{e}{V} \sum_{sj} Z_{ij}^{*s} u_j^s \quad (2)$$

$$P_i^{\text{E}} = \frac{1}{4\pi} \sum_j (\varepsilon_{ij}^{\infty} - \delta_{ij}) E_j, \quad (3)$$

where $\varepsilon_{ij}^{\infty}$ is the electronic component of the dielectric tensor, V is the bulk cell volume, ϵ_l the strain field, u_k^s the displacement of atom s from its equilibrium position; $e_{il}^{(0)}$ is the clamped-ion component of the piezoelectric tensor, and Z_{ik}^s the Born effective charge:

$$e_{il}^{(0)} = \left. \frac{\partial P_i^{\text{lat}}}{\partial \epsilon_l} \right|_u, \quad Z_{ik}^{*s} = \frac{V}{e} \left. \frac{\partial P_i^{\text{lat}}}{\partial u_k^s} \right|_{\epsilon}. \quad (4)$$

The spontaneous component of the polarization does not depend on strain and fields, and it is non-vanishing also in zero field. Using Eq. (2) and (3) we can rewrite Eq. (1) as

$$\varepsilon_{ij}^0 = \varepsilon_{ij}^{\infty} + 4\pi \sum_l e_{il}^{(0)} \frac{\partial \epsilon_l}{\partial E_j} \bigg|_u + \frac{4\pi e}{V} \sum_{sk} Z_{ik}^{*s} \frac{\partial u_k^s}{\partial E_j} \bigg|_{\epsilon} \quad (5)$$

We shall discuss first how the second and third term are evaluated, and then discuss the electronic dielectric tensor. The last two terms in Eq. (5) quantify the contributions of the macroscopic and microscopic structural

degrees of freedom to the total polarization, respectively. In the absence of other external perturbations, the strain field ϵ_l and the atomic displacement u_k^s are related to the screened field \mathbf{E} by the condition of vanishing stress,

$$\sigma_l = \sum_i e_{il} E_i - \sum_m \lambda_{lm} \epsilon_m = 0, \quad (6)$$

and vanishing Hellmann-Feynman forces,

$$F_i^s = e \sum_j Z_{ij}^{*s} E_j + V \sum_{ls} \Xi_{il}^s \epsilon_l - \sum_{js'} \Phi_{ij}^{ss'} u_j^{s'} = 0. \quad (7)$$

The quantities appearing in Eqs. (6) and 7 are the elastic constants

$$\lambda_{lm} = -\frac{\partial \sigma_l}{\partial \epsilon_m} - \sum_{is'} \frac{\partial \sigma_l}{\partial u_i^s} \frac{du_i^s}{d\epsilon_m}, \quad (8)$$

the piezoelectric tensor

$$\begin{aligned} e_{il} &= \frac{\partial P_i^{\text{lat}}}{\partial \epsilon_l} + \sum_{js} \frac{\partial P_i^{\text{lat}}}{\partial u_j^s} \frac{du_j^s}{d\epsilon_l} \\ &= e_{il}^{(0)} + \sum_{jks's'} Z_{ij}^{*s} \Phi_{jk}^{-1ss'} \Xi_{kl}^{s'}, \end{aligned} \quad (9)$$

and the harmonic force constants and internal strain parameters

$$\Phi_{ij}^{ss'} = -\left. \frac{\partial F_i^s}{\partial u_j^{s'}} \right|_{\epsilon}, \quad \Xi_{il}^s = \frac{1}{V} \left. \frac{\partial F_i^s}{\partial \epsilon_l} \right|_u. \quad (10)$$

Combining Eq. (6) and (7), we obtain u and ϵ as a function of the electric field:

$$u_i^s = \sum_{jks'} \Phi_{ik}^{-1ss'} \left(e Z_{kj}^{*s'} + V \sum_{lm} \Xi_{kl}^{s'} \lambda_{lm}^{-1} e_{mj} \right) E_j; \quad (11)$$

$$\epsilon_i = \sum_{jk} \lambda_{ik}^{-1} e_{kj} E_j. \quad (12)$$

These relations are the first two key ingredients of our method. Substituting them into Eq. (5), we obtain after some manipulation the following general expression for the static dielectric tensor:

$$\begin{aligned} \varepsilon_{ij}^0 &= \frac{4\pi e^2}{V} \sum_{klss'} Z_{ik}^{*s} \Phi_{kl}^{-1ss'} Z_{lj}^{*s'} \\ &\quad + 4\pi \sum_{mn} e_{im} \lambda_{mn}^{-1} e_{nj} + \varepsilon_{ij}^\infty \\ &= \varepsilon^a + \varepsilon^b + \varepsilon_{ij}^\infty. \end{aligned} \quad (13)$$

As implied by Eq. (6), this definition holds for fixed stress, certainly an experimentally relevant situation. The first term in the last equation is due to atomic displacements from the ideal position at fixed lattice parameter; the second is the contribution of piezoelectricity-related lattice constant changes; the third is the pure electronic dielectric screening for a frozen lattice system.

A central point of the above analysis is that all the ingredients of Eqs. (4) and (8–10) needed for Eq. (13) can be calculated from distorted and strained bulk cells using ab-initio total-energy and force calculations, supplemented by calculations of the dielectric polarization in zero field using the Berry-phase approach [1,3,4,6]. The only exception is the electronic dielectric constant ε^∞ , for which [6] an alternate approach has to be devised.

The electronic dielectric tensor – As we now show, ε^∞ can be obtained using the relationship between macroscopic polarization in zero field and charge accumulation at the interfaces of an appropriately built homojunction of the material of interest [7,8]. In an insulating superlattice consisting of periodically alternating slabs of equal length, stacked along direction $\hat{\mathbf{n}}$ and made of materials 1 and 2, the displacement field orthogonal to the interfaces is conserved: $D_1 = E_1 + 4\pi P_1(E_1) = E_2 + 4\pi P_2(E_2) = D_2$. (We use a scalar notation for the components of the vectors along $\hat{\mathbf{n}}$.) Expanding the polarization to first order in the screened fields in the two materials as $P_i(E) = P_i + \chi_i E_i$, with P_i the polarization in zero field and χ_i the susceptibility, one obtains

$$4\pi(P_2 - P_1) = \varepsilon_1^\infty E_1 - \varepsilon_2^\infty E_2.$$

In the absence of zero-field (e.g. spontaneous) polarization, the familiar equality $\varepsilon_1^\infty E_1 = \varepsilon_2^\infty E_2$ is recovered. To proceed, we note that periodic boundary conditions imply $E \equiv E_1 = -E_2$, and $\Delta E \equiv E_1 - E_2 = 2E$, so that

$$4\pi(P_2 - P_1) = \frac{1}{2}(\varepsilon_1^\infty + \varepsilon_2^\infty)\Delta E.$$

The charge accumulation per unit area at the interface between materials 1 and 2 is $s_{\text{int}} = \pm \Delta E / 4\pi$. Therefore, switching to an obvious vector notation,

$$s_{\text{int}} = \pm 2 \hat{\mathbf{n}} \cdot (\mathbf{P}_2 - \mathbf{P}_1) / (\varepsilon_1^\infty + \varepsilon_2^\infty), \quad (14)$$

which connects the macroscopic bulk polarizations $\mathbf{P}_{1,2}$ at zero field with the components $\varepsilon_{1,2}^\infty$ of the dielectric tensors of the interfaced materials along the interface normal $\hat{\mathbf{n}}$.

In an undistorted homojunction, i.e. a superlattice in which material 1 is identical to material 2, there is no interface, no polarization change can occur, and the interface charge is zero. However, a polarization difference can be generated in a controlled manner by inducing a small distortion δ of one of the atomic sublattices in half of the superlattice unit cell. The interface charge s_{int} accumulated at the interface between distorted and undistorted regions can be easily calculated via macroscopic averages [7,9]. The zero field polarizations \mathbf{P}_2 for the material in the undistorted state, and \mathbf{P}_1 for the material in the same strain state as in the superlattice, are evaluated directly using the Berry phase technique. From Eq. (14), one

then extracts the average electronic dielectric constant $\bar{\epsilon}^\infty = (\epsilon_1^\infty + \epsilon_2^\infty)/2$.

In principle ϵ_1 , the dielectric constant in the distorted state, differs from the actual dielectric constant ϵ_2 ; thus, so does $\bar{\epsilon}$. However, in the limit of zero distortion, $\bar{\epsilon}$ equals the component of the dielectric tensor along \hat{n} :

$$\epsilon^\infty = \lim_{\delta \rightarrow 0} \bar{\epsilon}.$$

This limit can be evaluated with essentially arbitrary accuracy by extrapolation or interpolation. The procedure just outlined, yielding the electronic dielectric constants, is the third key ingredient of the method.

In summary, in the present approach the static dielectric constant is calculated via (i) calculation of the elastic and force constants, (ii) calculation of the piezoelectric tensor and Born charges, (iii) evaluation of the electronic dielectric tensor. Task (i) requires standard total energy and stress calculations; tasks (ii) and (iii) use the geometric quantum phase polarization; task (iii) also uses relatively small, accurately controllable supercell calculations. In the latter, one must take care that (a) the slabs be short enough that the constant electric field will not cause metallization, and that (b) the slabs be sufficiently long to recover bulk-like behavior away from the interfaces. Both requirements are generally met even by materials with small calculated gaps for sufficiently small applied strains.

The quantities needed to evaluate the dielectric tensor are usually obtained by means of DFPT [5,10]. The novelty of the present method is in the absence of a perturbative approach, and in the determination of the electronic screening and piezoelectric properties using their connection with the geometric quantum phase.

Application to III-V nitrides – We now apply the formalism just developed to the calculation of $\epsilon_{33}^0|_a$, the component of the static dielectric tensor along the (0001) axis at fixed lattice constant a , for the wurtzite III-V nitrides AlN, GaN, and InN [11]. Besides serving as a test of our theory, this calculation provides to our knowledge the first ab initio theoretical prediction of the dielectric constant for these materials.

In the present case, only a few independent elements of the tensors described above are needed, namely those containing derivatives of the total energy and polarization with respect to the lattice constant c and the internal structure parameter u . The piezoelectric constant and the Born effective charge involved are

$$e_{33} = c_0 \left. \frac{\partial P_3}{\partial c} \right|_u + 2eZ_{33}^* \Phi_{33}^{-1} \Xi_{33}, \quad Z_{33}^* = \frac{\sqrt{3}a_0^2}{4e} \left. \frac{\partial P_3}{\partial u} \right|_c.$$

The force constant Φ_{33} (whence $\Phi_{33}^{-1} = 1/\Phi_{33}$ is obtained) and the internal strain parameter Ξ_{33} are calculated as derivatives of the Hellmann-Feynman force F_3 with respect to an atomic displacement from equilibrium,

and to a homogeneous strain of the lattice structure, respectively:

$$\Phi_{33} = c_0^{-1} \left. \frac{\partial F_3}{\partial u} \right|_c, \quad \Xi_{33} = \frac{4}{\sqrt{3}a_0^2} \left. \frac{\partial F_3}{\partial c} \right|_u.$$

The relevant inverse elastic constant is $\lambda_{33}^{-1} = 1/\lambda_{33}$, where

$$\lambda_{33} = c_0 \frac{\partial \sigma_3}{\partial c} - V \Xi_{33} \Phi_{33}^{-1} \Xi_{33}.$$

All calculations are done using density functional theory in the local density approximation (LDA) to describe the exchange and correlation energy, and ultrasoft pseudopotentials [12] for the electron-ion interaction. A plane-wave basis cut off at 25 Ry and 12-point Chadi-Cohen [13] mesh are found to give fully converged values for the bulk properties. Given their known importance [14], the semicore d states of Ga and In are included in the valence. The piezoelectric tensor and Born charges have been calculated [4] via the Berry phase technique [1,6] using a 16-point Monkhorst-Pack [15] k-point mesh in the a -plane direction and 10 point uniform mesh in the c direction, testing convergence up to 360 total points. For the ϵ^∞ supercell calculation, we have employed (0001)-oriented superlattices of typically 4 formula units (16 atoms), and typical cation sublattice displacements along (0001) of 1-2 % of the bond length for AlN and GaN. Smaller displacements (~ 0.3 %) were used for InN. 25 Ry cutoff and 12 k-points in the irreducible superlattice Brillouin zone guarantee convergence. No ionic relaxation is allowed, so that the response is purely electronic.

We report in Table I the calculated dielectric constants and their various components as given by Eq. (13) for AlN, GaN, and InN, along with the available experimental data [16–18]. The electronic dielectric constants are very close to the experimental values for both AlN and GaN, slightly larger for InN. The calculated static constant agrees well with experiment for GaN, the only one for which it is available experimentally. We also list the values of the various constants contributing to ϵ^0 in Table II. For AlN and GaN, the structural constants are similar, while the piezoelectric coefficient e_{33} is much higher in AlN. InN behaves somewhat differently, as expected from previous experience on other In compounds [5].

Discussion – In homopolar semiconductors, the external field does not cause distortions of the crystal lattice, so that the static dielectric constant coincides with the electronic one; our method as outlined above is not applicable in this case, since no zero-field polarization can exist in these materials. It does apply, however, to all heteropolar materials, in which a polarization can always be induced by appropriate atomic displacements. Apart from the electronic response, a lower crystal symmetry such as in wurtzites enables the action of screening mechanisms related to lattice distortions. As apparent from

of Eq. (13), the difference among ϵ^0 and ϵ^∞ is due to the polarization induced by optically-active lattice vibrations (as quantified by the dynamical charges), and to the piezoelectric response, if any, along the appropriate axis (as measured by the piezoelectric constants). In a previous work [4] we have shown that AlN, GaN, and InN have large effective charges, and the highest piezoelectric coefficients amongst all tetrahedrally bonded semiconductors. Indeed (see Table I), the difference between static and high-frequency dielectric constants is large: in III-V nitrides the phonon-related term is comparable to the electronic one, and the piezoelectric component is about 10% of each of the other two. An important point to be noted is that the piezoelectric contribution cannot be neglected in an accurate calculation. This will be even more important in materials with large piezoelectric constants, such as ferroelectric perovskites.

In conclusion, we have presented a novel procedure for the calculation of the dielectric tensor based on the geometric quantum phase polarization theory. The method only uses bulk calculation, with the exception of a small supercell calculation, needed in the determination of the electronic dielectric constant. As an application, we have provided the first ab initio prediction of the dielectric constants of wurtzite AlN, GaN, and InN.

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$$\Delta \mathbf{P}_e = -\frac{2e}{(2\pi)^3} \int_{\lambda_1}^{\lambda_2} d\lambda \int_{BZ} d\mathbf{k} \frac{\partial^2}{\partial \lambda \partial \mathbf{k}'} \phi^{(\lambda)}(\mathbf{k}, \mathbf{k}') \Big|_{\mathbf{k}'=\mathbf{k}},$$

where

$$\phi^{(\lambda)}(\mathbf{k}, \mathbf{k}') = \text{Im}[\ln(\det S^{(\lambda)}(\mathbf{k}, \mathbf{k}'))]$$

is the geometric quantum Berry phase, and

$$S_{mn}^{(\lambda)}(\mathbf{k}, \mathbf{k}') = \langle u_m^{(\lambda)}(\mathbf{k}) | u_n^{(\lambda)}(\mathbf{k}') \rangle$$

is the overlap matrix of lattice periodic wavefunctions $u^{(\lambda)}$ at different crystal momenta. Since the adiabatic transformation should leave the system insulating, the method does not allow a direct determination of ϵ^∞ .

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TABLE I. Calculated high-frequency and static dielectric constant in AlN, GaN, and InN compared with available experimental data (in parenthesis). ϵ^a and ϵ^b are the first and second terms in Eq. (13) respectively, and $\epsilon_{33}^0 = \epsilon^a + \epsilon^b + \epsilon_{33}^\infty$.

	ϵ^a	ϵ^b	ϵ_{33}^∞	ϵ_{33}^0
AlN	5.06	0.64	4.61 (4.68 ^a)	10.31 —
GaN	4.44	0.15	5.69 (5.70 ^b)	10.28 (10.4 ^c)
InN	5.51	0.61	8.49 (8.40 ^b)	14.61

^aFrom Ref. [16], ^bRef. [17] and ^cRef. [18].

TABLE II. Constants needed in the evaluation of ε^0 in AlN, GaN, and InN (see text).

	e_{33}	Z_{33}^*	Φ_{33}	Ξ_{33}	λ_{33}
units	C/m ²	—	N/m	10 ²¹ N/m ³	10 ¹¹ N/m ²
AlN	+1.462	-2.70	+204	+0.45	+3.81
GaN	+0.727	-2.72	+209	+0.38	+3.80
InN	+1.092	-3.02	+155	+0.32	+2.22